



Electrically enhanced adsorption and green regeneration for fluoride removal using $\text{Ti}(\text{OH})_4$ -loaded activated carbon electrodes

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ABSTRACT

An electrically enhanced fluoride removal method was developed that blended the merits of electrosorption and adsorbent adsorption. This method has the advantages of high adsorption selectivity and capacity for fluoride. The saturated adsorption capacity of $\text{Ti}(\text{OH})_4$ for fluoride in the electrode of $\text{Ti}(\text{OH})_4$ -loaded activated carbon reached 115.2 mg/g when a voltage of +1.2 V was applied to the electrode. The electrode was easily and cleanly regenerated in a short time in aqueous solution with high fluoride concentrations when a voltage of -1.6 V was applied. The adsorption capacity of the $\text{Ti}(\text{OH})_4$ -loaded electrode for fluoride did not decrease after multiple cycles of electrically enhanced adsorption and regeneration. Excellent adsorption selectivity for fluoride was achieved. The electrically enhanced adsorption method showed potential for fluoride removal.

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1. Introduction

Fluorine is a necessary trace element for the human body, which helps enhance the strength of teeth and bones. However, excessive intake of the fluoride ion is harmful to health (Tomar and Kumar, 2013; Chen et al., 2009). The fluoride that enters the body mainly comes from drinking water; the fluoride concentration recommended by the World Health Organization (WHO) is 0.5–1.5 mg/L (Bruce, 1986). However, the fluoride concentration in groundwater is often higher than this value (Bhatnagar et al., 2011). For example, fluoride concentrations in the groundwater of some villages in China exceed 8 mg/L (Anonymous Drinking water atlas of China, 1990), and in some areas of India, they reach 30 mg/L (Handa, 1975).

Adsorbent adsorption is the most widely used method for fluoride removal from drinking water, and many adsorbents have been synthesized (Mohapatra et al., 2009; Fan et al., 2003). Metal oxide adsorbents, such as nano-alumina (Wang et al., 2009) and granular ferric hydroxide (Kumar et al., 2009), have high adsorption capacities. Rare earth metals, such as iron-aluminum-cerium (Zhao et al., 2012), cerium-titanium (Deng et al., 2010), and manganese-cerium (Deng et al., 2011), are also often used for increasing the adsorption capacity. These chemical adsorbents have high adsorption capacities for fluoride. However, the regeneration of the exhausted adsorbent presents a problem. Because fluoride is usually chemically adsorbed on the adsorbents, alkali, acid, or salt-solution washing must be performed to

regenerate the adsorbent, producing a large quantity of waste water and causing secondary pollution to the environment. In addition, the fluoride adsorption capacity of the adsorbent decreases significantly after several cycles of adsorption and regeneration.

Electrosorption is a clean and economical method for desalination, in which regeneration can be easily achieved by shorting the electrodes without adding any chemicals (Chao et al., 2015). Carbon materials with high specific surface areas, such as activated carbon (AC) (Yeh et al., 2015; Chen et al., 2015; Choi, 2010), carbon fibers (Wang et al., 2012; Chen et al., 2014), carbon aerogels (Xu et al., 2008), carbon nanotubes (Tofighy and Mohammadi, 2010), graphene (Li et al., 2009, 2010), mesoporous carbon (Tsouris et al., 2011), carbon composite materials (Zhang et al., 2012a), and biomass carbonaceous aerogels (Li et al., 2017a) have been used as electrodes for electrosorption. Positive and negative carbon electrodes can be assembled in electrosorption cells. When aqueous solutions flow through the gap between the electrodes, cations move to the negative electrode and anions to the positive electrode in the electric field, forming an electric double layer near the electrode surface. The ions in the solution move to the electrode surface and enrich the electric double layer, decreasing the ion concentration of the bulk solution (Porada et al., 2013). Electrosorption has the advantages of high energy efficiency, high removal efficiency, low cost, and easy regeneration. In a previous work, electrosorption with micropore-dominant AC as an electrode showed an excellent adsorption performance for fluoride in the absence of other competitive anions (Li et al., 2017b). Tang et al. (2015) investigated the fluoride removal performance in the existence of competitive chloride; the fluoride removal efficiency was much lower than that of the chloride, and electrosorption selectivity for fluoride was not dis-

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cussed. In fact, electrosorption with carbon electrodes does not permit adsorption selectivity for fluoride. Our previous work (Li et al., 2016) also showed that electrosorption had the lowest removal efficiency for fluoride compared to that for other anions. Coexisting anions such as bicarbonate, sulfate, and phosphate significantly reduce the fluoride removal efficiency during electrosorption, causing almost no fluoride removal. When electrosorption is used for fluoride removal, it removes more of the other anions, resulting in high energy consumption.

Adsorbent adsorption can achieve high adsorption capacity and selectivity for fluoride, but suffers from problems in regenerating the exhausted adsorbent. Electrosorption can achieve clean regeneration, but without selectivity for fluoride. An ideal fluoride removal method would combine the superiorities of adsorbent adsorption and electrosorption, having high adsorption selectivity, high adsorption capacity, and clean regeneration. Loading chemical adsorbent on the carbon material for a conductive composite electrode is a potential way for fluoride removal with high selectivity and clean regeneration. The chemical adsorbent in the composite electrode provides the adsorption selectivity for fluoride, and the clean regeneration is supposed to be achieved by applying a negative voltage on the composite electrode. However, few reports have discussed the combination of adsorbent with electrode for removing fluoride or other ions. Wu et al. (2016) studied electrosorption of fluoride on a TiO_2 -loaded AC electrode, in which the saturated Langmuir adsorption capacity was very low at only 3.0 mg/g, and the adsorption selectivity for fluoride and regeneration process was not discussed.

Titanium hydroxide is an excellent adsorbent for fluoride ions with high selectivity, and the selectivity for fluoride comes from the ion exchange between the fluoride ion and the surface hydroxyls of the titanium hydroxide (Wajima et al., 2009; Ishihara et al., 2002). AC is widely used to prepare electrodes because of its high conductivity and high specific surface area. In this study, hydrous titanium dioxide was loaded on AC to prepare a composite electrode for fluoride electrosorption with high selectivity. The fluoride removal and regeneration performance by this composite electrode was studied.

2. Materials and methods

2.1. $\text{Ti}(\text{OH})_4$ loading on AC

A 100-mL solution of titanium sulfate (analytical purity, Beijing Chemical Reagents, China) at a concentration of 0.5 mol/L was prepared, and 10 g AC powder (Fuzhou Yi-Huan Carbon, China) was added to the solution. The suspension was ultrasonically treated for 1 h to enhance the impregnation of titanium ions in the micro-porous AC. For loading the titanium hydroxide on the AC surface, titanium sulfate in the suspension (pH=0.63) was hydrolyzed by titrating a sodium hydroxide solution until the suspension pH reached 4.0. Thereafter, the suspension was aged for 2 h, and then centrifuged, obtaining a $\text{Ti}(\text{OH})_4$ -loaded AC adsorbent (Ti-AC). The composited Ti-AC adsorbent was washed using deionized water and centrifuged repeatedly for four times to remove soluble salts from the adsorbent surface. The composited Ti-AC adsorbent was dried at 100 °C for 12 h.

The loading amount of titanium hydroxide in the Ti-AC was measured by thermogravimetric analysis. The Ti-AC adsorbent was heated to 900 °C at a heating rate of 10 K/min under an oxygen atmosphere. The activated carbon was burned out, and the titanium hydroxide turned into titanium dioxide. The thermogravimetric analysis curve is shown in Fig. SM-1, and the percentage of titanium hydroxide in

the Ti-AC adsorbent was calculated to be 29% from the percentage of titanium dioxide.

2.2. Fabrication of electrodes

The electrode fabrication and raw material ratio were the same as our previous work (Li et al., 2016). A slurry was prepared by mixing Ti-AC powder, carbon black (Fuzhou Yi-Huan Carbon, China), and a solution of poly(vinylidene fluoride) (PVDF, MW=275000, Sigma-Aldrich, USA) dissolved in dimethylacetamide (DMAc, Beijing Chemical Reagents, China). The slurry was stirred for 3 h to obtain a homogeneous mixture and then coated on a graphite plate. The Ti-AC adsorbent, carbon black as the conductive material, and PVDF as the binder had the fraction ratio of 8:1:1. The coated plate was dried in an oven at 80 °C for 6 h and then placed in a vacuum oven at 50 °C for 2 h to completely remove any organic solvent remaining in the micropores of the electrodes, obtaining a Ti-AC electrode. A blank AC electrode (without $\text{Ti}(\text{OH})_4$) was also prepared using the same method, in which the fraction ratio of AC, carbon black, and PVDF was also 8:1:1. The Ti-AC and AC electrodes were then assembled into an electrosorption cell as the working and counter electrodes, respectively.

2.3. Apparatus and electrosorption

A schematic of the electrosorption apparatus is shown in Fig. 1. The electrosorption cell includes two electrodes, i.e., the Ti-AC electrode used as the working electrode for fluoride adsorption and the AC electrode used as the counter electrode for cation adsorption, and the spacing between the two electrodes is 2 mm. The electrode has a dimension of 80 × 80 mm. A hole with a diameter of 6 mm was opened on the electrodes for water to flow through. During the electrosorption process, the solution was fed through a peristaltic pump into the electrosorption cell, and the flow rate was controlled at 10 mL/min, then the effluent was returned to the feed tank, and the solution volume was 50 mL. In the electrosorption, the Ti-AC electrode was positively charged and the AC electrode was negatively charged. In the regeneration process, the positive and negative electrodes were reversely applied. The experiments were conducted at 25 °C, and no obvious changes of temperature were observed during the experiment.

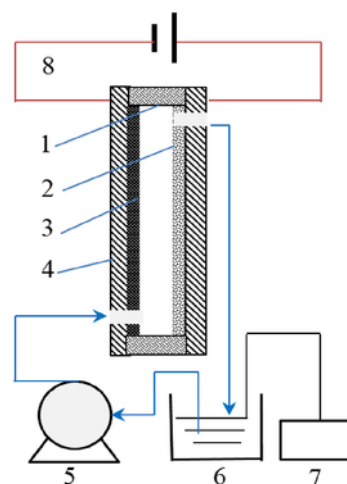


Fig. 1. Schematic of the experimental apparatus for electrosorption. 1. Insulated spacer; 2. Ti-AC electrode; 3. AC electrode; 4. Graphite plate; 5. Peristaltic pump; 6. Feed tank; 7. Fluoride ion-selective electrode; 8. Potentiostat.

In the electrosorption process, the solution was circulated until the electrosorption reached equilibrium. The fluoride concentration was measured using a fluoride ion-selective electrode. The equilibrium electrosorption capacity was defined as

$$Q_e (\text{mg/g}) = \frac{(C_0 - C_e) V}{m} \quad (1)$$

where Q_e is the equilibrium electrosorption capacity, mg/g (Ti-AC); C_0 and C_e are the initial and equilibrium fluoride concentrations, respectively, mg/L; V is the volume of the circulated solution, L, i.e., 50 mL in this work; and m is the mass of Ti-AC on the composite electrode, g.

3. Results and discussion

3.1. Structure and morphology of Ti-AC adsorbent

A scanning electron microscopy (SEM) image of the Ti-AC adsorbent is shown in Fig. SM-2. It is shown that some $\text{Ti}(\text{OH})_4$ nuclei are coated on the outer surface of AC. It is noted that most of the outer surface of AC is not covered with $\text{Ti}(\text{OH})_4$ nuclei. This enables contact between conductive AC particles to form a conductive network in the Ti-AC electrode, which provides the Ti-AC electrode with high conductivity, increasing the adsorption and regeneration efficiency of fluoride.

The X-ray diffraction (XRD) was used to characterize the Ti-AC adsorbent, and the result is shown in Fig. SM-3. It indicates that the Ti-AC adsorbent has a weak and broad peak near the 2θ of 25.3, which is assigned to the titanium hydroxide adsorbent as synthesized in literature (Wajima et al., 2009). According to the literature (Ishihara et al., 2002), titanium hydroxide was stable at 200 °C, and began to transform into crystalline titanium dioxide when the temperature reached 300 °C. Since the titanium hydroxide obtained in this work was at 80 °C, so titanium hydroxide is loaded on the AC, forming a Ti-AC adsorbent.

The Brunauer-Emmett-Teller (BET) specific surface areas of AC and Ti-AC were measured by nitrogen adsorption at 77 K. The nitrogen adsorption isotherms of AC and Ti-AC are shown as Fig. SM-4. The specific surface areas of the AC and Ti-AC adsorbents are 2200 m²/g and 1700 m²/g respectively, while that of $\text{Ti}(\text{OH})_4$ precipitates prepared in the same procedures is only 25 m²/g. It is inferred that $\text{Ti}(\text{OH})_4$ is distributed on the inner and outer surfaces of AC. The high specific surface area of the Ti-AC adsorbent is favorable to adsorb fluoride.

The pore size distribution was calculated by density functional theory from the nitrogen adsorption isotherm. The pore size distributions of the AC and Ti-AC are shown in Fig. 2. The characteristic pore sizes of AC are 1.56 nm and 2.43 nm, while those of the Ti-AC adsorbent are 1.50 nm and 2.35 nm, respectively. The decrease in the characteristic pore size (0.06 nm and 0.08 nm) also indicates that $\text{Ti}(\text{OH})_4$ is coated on the inner surface of the AC, enabling a high adsorption capacity for fluoride by Ti-AC.

3.2. Fluoride removal performance of $\text{Ti}(\text{OH})_4$ and Ti-AC adsorbent

For different initial fluoride concentrations, adsorbents with masses of 50 mg were added to 50 mL of fluoride solutions for adsorption until adsorption equilibrium was reached. The equilibrium fluoride concentration was measured using the fluoride ion-selective electrode and then the equilibrium adsorption capacity was calculated.

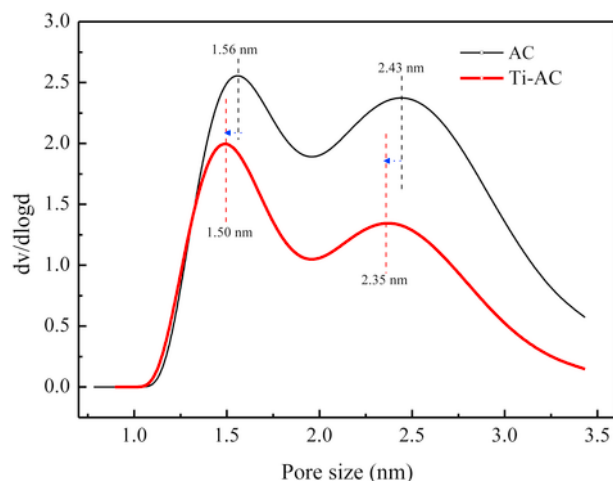


Fig. 2. Pore size distributions of AC and Ti-AC adsorbent.

The fluoride adsorption isotherms of the $\text{Ti}(\text{OH})_4$ and Ti-AC adsorbents are measured and shown in Fig. 3. In each adsorption experiment, the initial solution pH was about 6–8 and the solution pH decreased to about 3.5–4.0 after adsorption equilibrium. The Langmuir and Freundlich models are used to fit the fluoride adsorption isotherms. It is shown that the Langmuir model fits the experimental results better for both the $\text{Ti}(\text{OH})_4$ and Ti-AC adsorbents, implying the monolayer adsorption of fluoride on the adsorbent surface. The fitted parameters of the adsorption isotherms are listed in Table SM-1.

As shown in Table SM-1, the $\text{Ti}(\text{OH})_4$ and Ti-AC adsorbents have saturated fluoride adsorption capacities of 31.0 mg/g and 18.0 mg/g, respectively. The activated carbon used in this work has very little adsorption capacity for fluoride, which has been studied in our previous work (Li et al., 2017b). Therefore, the adsorption capacity for fluoride of the Ti-AC adsorbent was resulted from the $\text{Ti}(\text{OH})_4$ that loaded on AC. Considering the 29% loading of $\text{Ti}(\text{OH})_4$, the saturated adsorption capacity of $\text{Ti}(\text{OH})_4$ in the Ti-AC adsorbent is 62.1 mg/g, which is much higher than that of the $\text{Ti}(\text{OH})_4$ adsorbent. The $\text{Ti}(\text{OH})_4$ precipitation on the abundant surface of the AC gives a high specific surface area of 1700 m²/g for the Ti-AC adsorbent, while the specific surface area is only 25 m²/g for the

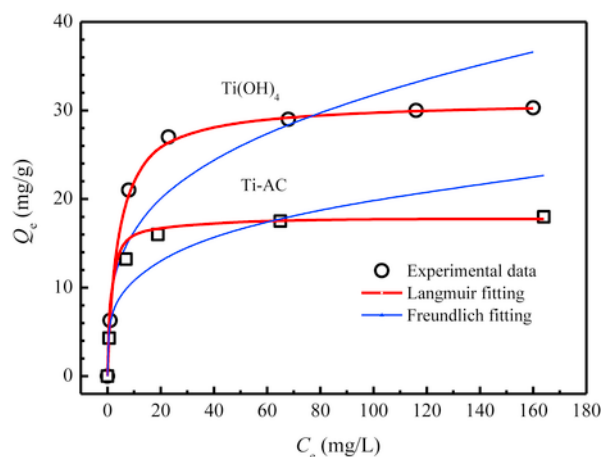


Fig. 3. Fluoride adsorption isotherms of $\text{Ti}(\text{OH})_4$ and Ti-AC adsorbents.

Ti(OH)₄ adsorbent in the absence of the AC. The high specific surface area of Ti(OH)₄ on the Ti-AC adsorbent surface provides more adsorption sites for fluoride ions.

3.3. Electrically enhanced fluoride adsorption and regeneration

Electrosorption with the Ti-AC electrode was conducted to examine the effect of positive voltage on the fluoride adsorption capacity. The initial fluoride concentration was set at 50 mg/L, and a positive voltage of 1.2 V was applied to the Ti-AC electrode. For comparison, adsorption was also conducted without an applied voltage. The adsorption performance curves are shown in Fig. 4. It shows that the fluoride concentration gradually decreases and finally reaches adsorption equilibrium in both situations. The fluoride adsorption rate under a voltage of +1.2 V is higher and the equilibrium fluoride concentration is lower than those for adsorption without the applied voltage. A higher fluoride adsorption capacity is obtained when the voltage applied is +1.2 V. The fluoride adsorption curve is fitted using the pseudo-first-order kinetics model, with fitting results as shown in Table SM-2.

Table SM-2 shows that the fluoride adsorption curves of the Ti-AC electrode are well fitted using the pseudo-first-order kinetic model, with correlation coefficients of 0.987 and 0.992 under the applied voltages of 0 and +1.2 V, respectively. When a voltage of +1.2 V is applied to the Ti-AC electrode, the equilibrium fluoride concentration is decreased from 16.9 mg/L to 10.4 mg/L, increasing the equilibrium fluoride adsorption capacity. The adsorption rate constant k is increased from 0.0117 min⁻¹ to 0.0131 min⁻¹, indicating an increase in the adsorption rate. After electrosorption for 300 min, the solution kept clear and no Ti-AC particle was observed in the solution, which indicated the Ti-AC electrode had a good mechanical stability.

The fluoride adsorption isotherm of the Ti-AC electrode under the voltage of +1.2 V is also measured as shown in Fig. SM-5. The isotherm also fits the Langmuir model well, with a correlation coefficient of 0.999. The fitting results by the Langmuir and Freundlich models are listed in Table SM-3.

The saturated Langmuir adsorption capacity of the Ti-AC adsorbent for fluoride was 18.0 mg/g, in which the capacity of Ti(OH)₄ was calculated to be 62.1 mg/g when no positive voltage was applied. However, after applying a voltage of +1.2 V on the Ti-AC electrode,

the saturated Langmuir adsorption capacity of Ti-AC for fluoride was increased to 33.6 mg/g (Ti-AC), from which the fluoride adsorption capacity of Ti(OH)₄ was calculated to be 115.2 mg/g. This shows that the fluoride adsorption capacity of Ti(OH)₄ adsorbent increases in two stages: first, loading Ti(OH)₄ onto the AC surface increases the adsorption capacity from 31.0 mg/g to 62.1 mg/g; second, applying a voltage of +1.2 V on the Ti-AC electrode further increases the capacity to 115.2 mg/g, which is a high saturated fluoride adsorption capacity compared to most chemical adsorbents.

When a voltage of +1.2 V was applied to the Ti-AC electrode, an electric field formed between the Ti-AC and AC electrodes, and the negatively charged fluoride ions moved faster to the positive Ti-AC electrode. The electrical double layer was formed and enhanced by the applied positive voltage, and the fluoride ions accumulated in the electrical double layer of the positive Ti-AC electrode. Then the fluoride concentration on the Ti-AC electrode surface was increased, leading to the high adsorption capacity for fluoride ions. At low fluoride concentrations, fluoride is concentrated on the electrode surface due to the positive voltage, so high adsorption capacity is obtained, which makes the fluoride concentration of effluent easy meet the WHO standards.

To examine the regeneration performance of the Ti-AC electrode, multiple cycles of electrosorption-regeneration were conducted by applying a voltage of +1.2 V in electrosorption and a voltage of -1.6 V in regeneration. In the designed experiment, the electrosorption was run for 80 min at +1.2 V first, and then the regeneration was run for 15 min at -1.6 V. Thereafter, the electrosorption was run for 60 min, before running regeneration for 15 min, for four cycles. The first cycle of 80 min was set to investigate the electrosorption performance, and the shorter time of the subsequent cycles was set to investigate the multi-regeneration performance. To examine the effect of negative voltage on the regeneration, regeneration without an applied voltage was conducted for 120 min, and then a voltage of -1.6 V was applied again to confirm the effects of the voltage. The multiple cycles of electrosorption-regeneration performance are shown in Fig. 5.

Fig. 5 shows that almost 80% of the adsorbed fluoride is desorbed in 15 min when a voltage of -1.6 V is applied to the Ti-AC electrode. The desorption process enhanced by the voltage of -1.6 V is faster than the adsorption. In each electrosorption in the subsequent cycles, the fluoride concentration is decreased to about 23 mg/L, indicating that the adsorption capacity does not decrease. In the first regenera-

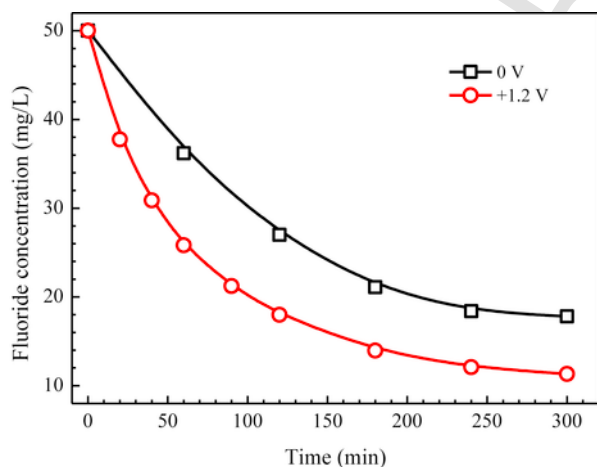


Fig. 4. Enhanced fluoride adsorption of Ti-AC electrode under a voltage of +1.2 V (Initial fluoride concentration: 50 mg/L, initial pH: 6.5).

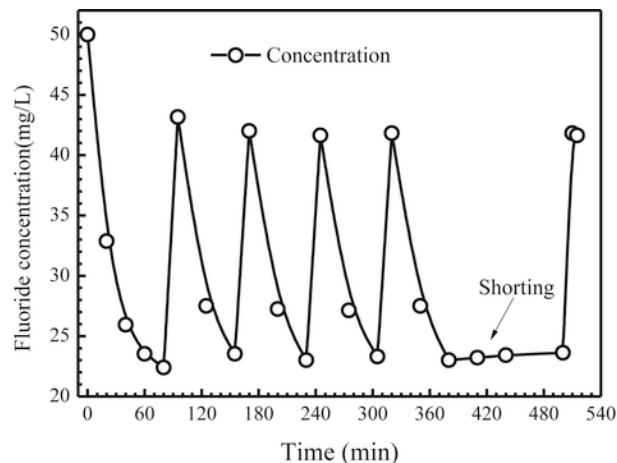


Fig. 5. Multiple cycles of electrosorption-regeneration performance using Ti-AC electrode (Initial fluoride concentration: 50 mg/L, electrosorption voltage: +1.2 V, regeneration voltage: -1.6 V).

tion of the Ti-AC electrode, the fluoride concentration of the solution reached 42 mg/L, lower than the initial fluoride concentration of 50 mg/L, which indicates that some fluoride adsorbed on the Ti-AC surface with poor conductivity was not desorbed. In the subsequent regeneration cycles, the fluoride concentration reached about 42 mg/L, which indicates that almost 100% of the newly adsorbed fluoride was released, while the fluoride not released from the Ti-AC electrode in the first regeneration cycle was still remained.

For the regeneration by shorting the electrodes from 380 min to 500 min, no fluoride ion release is detected. However, once a voltage of -1.6 V is applied to the Ti-AC electrode at 500 min, the fluoride is desorbed in 15 min, indicating that the negative voltage provides the driving force for the fluoride ions to overcome chemical bonding on the Ti-AC electrode. Theoretically, a higher voltage desorbs fluoride faster and more completely in the regeneration. Considering the electrosorption is a slow process, which takes about 300 min to reach the adsorption equilibrium in the experiments, and the water electrolysis voltage is 1.29 V, the adsorption voltage was set at $+1.2$ V to avoid the water electrolysis in the long-time electrosorption process. Meantime, for a fast regeneration and a higher fluoride desorption efficiency, the regeneration voltage was set at -1.6 V, in which the regeneration time is 15 min. Water electrolysis was not observed at the voltage of -1.6 V because of the surface resistance of the electrode. Higher voltage would cause water electrolysis. Therefore, a voltage of -1.6 V was applied for the regeneration of the Ti-AC electrode.

It should be noted that no chemicals are used in the regeneration process. The electrically enhanced regeneration is an efficient and clean method compared to traditional adsorbent regeneration using alkali and acid solutions. After five cycles of electrosorption–regeneration, as shown in Fig. 5, the adsorption capacity does not decrease. However, in traditional regeneration processes, the adsorption capacity usually decreases, e.g., the adsorption capacity decreases from 17.6 mg/g to 10.34 mg/g for a composite adsorbent after six cycles of desorption–adsorption (Zhang et al., 2012b).

The solution pH was also monitored simultaneously during the adsorption–desorption process. According to the literature (Wajima et al., 2009), the titanium hydroxide adsorbent had its highest adsorption capacity for fluoride when the solution pH is at about 3. The pH change during the electrosorption and regeneration process is shown in Fig. SM-6, in which the solution pH is in the range of 3.0–4.2, which is close to the optimum pH of the titanium hydroxide adsorbent. This makes Ti-AC electrode has a high adsorption capacity for fluoride. From the pH change, the adsorption and regeneration mechanism is analyzed. In the electrosorption process the solution pH increased from about 3.0 to 4.2, which is because the fluoride ion was adsorbed to the electrode surface and the hydroxyl was exchanged to the bulk solution, causing the pH increase. In the regeneration process, the fluoride ion was released to the bulk solution, and the hydroxyl was adsorbed to the adsorbent surface, thus causing the pH decrease. This confirms that the fluoride adsorption of titanium hydroxide is the ion exchange between the fluoride ion and hydroxyl (Wajima et al., 2009).

3.4. Selectivity of the electrically enhanced adsorption for fluoride

In order to investigate the adsorption selectivity of the Ti-AC electrode for fluoride, solutions containing different competitive anions were prepared. Cl^- , NO_3^- , or SO_4^{2-} was used as the competitive anion during fluoride adsorption. In the mixing solutions of F^-/Cl^- , F^-/NO_3^- , or $\text{F}^-/\text{SO}_4^{2-}$, the initial fluoride concentration was set at 10 mg/L, and the molar concentration of the competitive anion was set at 20 times that of the fluoride. For comparison, a solu-

tion containing only fluoride of 10 mg/L without other competitive anions was also used in the electrosorption. The fluoride concentration is relatively very low because the concentration of the competitive anion is 20 times higher. However, the adsorption capacity and adsorption rate for fluoride in the electrosorption process do not decrease, compared to those observed for the fluoride solution in the absence of competitive anions, as shown in Fig. 6. The competitive anions of Cl^- , NO_3^- , or SO_4^{2-} do not affect the fluoride adsorption performance of the Ti-AC electrode. The Ti-AC electrode maintains high adsorption selectivity for fluoride even with competitive anions present at high concentrations. The experimental results indicated that the concentrations of competitive anions, which significantly affect the TDS, have no influence on the fluoride removal performance. The Ti-AC electrode combines the advantages of adsorbent adsorption and electrosorption, providing promising adsorption selectivity for fluoride and a clean regeneration process without any use of chemicals. Due to the excellent performance, it is inferred that the electrosorption using Ti-AC electrode enables the fluoride removal from drinking water to meet the WHO recommended standards of 1.5 mg/L.

The AC electrode has poor electrosorption selectivity for fluoride when competitive anions presented. To verify that the fluoride adsorption selectivity is from the titanium hydroxide adsorbent, rather than the AC electrode, the fluoride adsorption selectivity experiment was conducted with AC electrode without the titanium hydroxide adsorbent loaded. The results are shown in Fig. SM-7. The fluoride solution with concentration of 10 mg/L was mixed with sodium chloride solution with a high concentration of 10 mmol/L, and the molar concentration of chloride ion was nearly 20 times higher than that of fluoride ion. The fluoride removal efficiency was nearly 0 and the removal efficiency of chloride ions was about 15%, indicating that the electrosorption of AC electrode has no adsorption selectivity for fluoride. However, the fluoride removal efficiency using the Ti-AC electrode reached 60% under the same conditions, confirming that the Ti-AC electrode has high adsorption selectivity for fluoride.

The fluoride adsorption and desorption processes for the Ti-AC electrode are illustrated in Fig. 7. Without an applied positive voltage, the $\text{Ti}(\text{OH})_4$ in the Ti-AC electrode adsorbs fluoride with high adsorption selectivity and reaches equilibrium at a relatively low fluoride concentration in the bulk solution. When a positive voltage is applied to the Ti-AC electrode, the anion motion to the positively charged Ti-AC electrode is enhanced, which increases the fluoride concentration near the electrode surface, reaching a high equilibrium

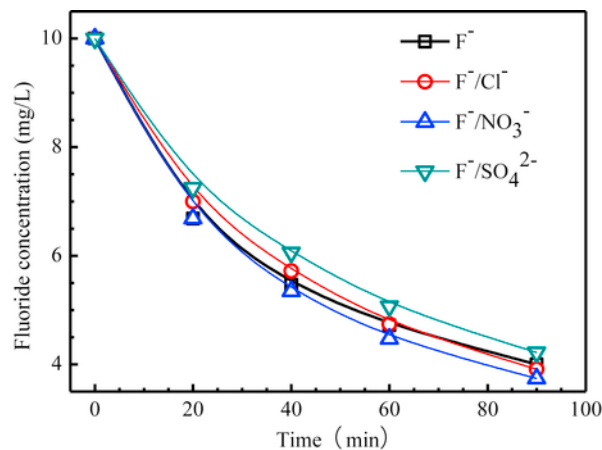


Fig. 6. Fluoride selective adsorption using Ti-AC electrode (Initial fluoride concentration: 10 mg/L, competitive anions concentration: 10 mmol/L, electrosorption voltage: $+1.2$ V).

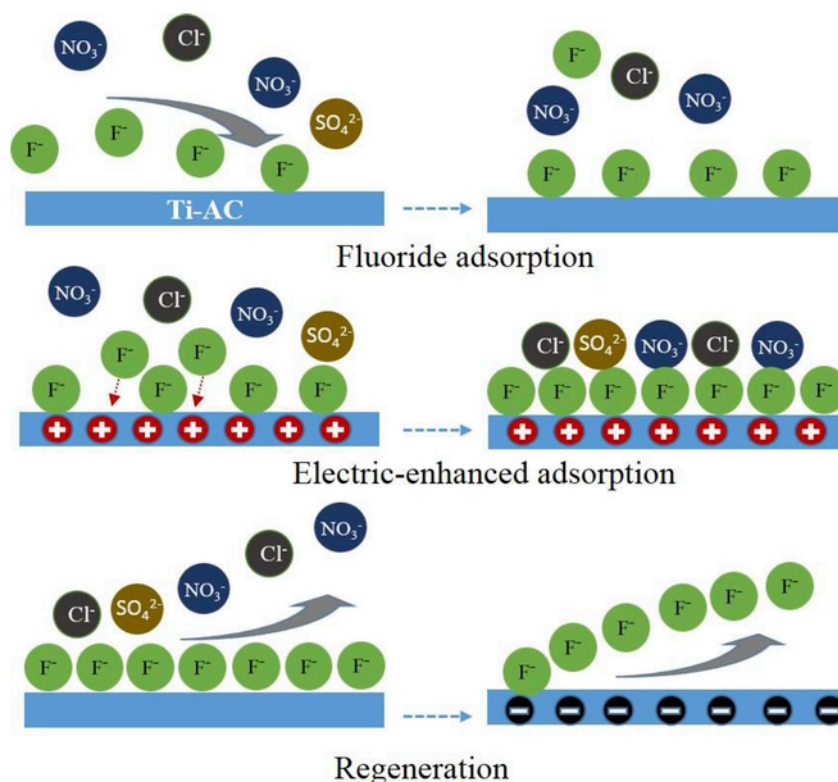


Fig. 7. Schematic of electrically enhanced specific adsorption for fluoride and adsorbent regeneration.

adsorption capacity because of the high fluoride concentration near the surface. In the regeneration process, shorting the electrodes can only release ions that have no chemical bonding with the electrode, and the chemically adsorbed fluoride cannot be released. During the regeneration process, when a negative voltage is applied to the Ti-AC electrode, a repulsive electric field is formed on the electrode surface, and the fluoride ion on the electrode surface was repulsed by the electric field. If the electrostatic force that acted on the Ti-AC electrode surface is greater than chemical adsorption, the chemically adsorbed fluoride ions are released. Therefore, the regeneration of the Ti-AC electrode can be easily achieved by applying a negative voltage, which is a clean and pollution-free process.

4. Conclusions

A novel electrosorption method for fluoride removal from drinking water was developed using a Ti-AC electrode, in which the $\text{Ti}(\text{OH})_4$ adsorbent was distributed on porous AC. The electrically enhanced adsorption method combined the advantages of adsorbent adsorption and electrosorption, yielding high adsorption selectivity for fluoride in aqueous solutions with high concentrations of competitive chlorides, nitrates or sulfates, and clean adsorbent regeneration without any use of chemicals.

By applying a voltage of +1.2 V on the Ti-AC electrode, faster adsorption with high selectivity and a high adsorption capacity for fluoride was achieved. The fluoride adsorption capacity of the $\text{Ti}(\text{OH})_4$ adsorbent in the Ti-AC electrode was enhanced in two stages. The first is the loading of $\text{Ti}(\text{OH})_4$ onto the AC surface, by which the capacity was increased from 31.0 mg/g to 62.1 mg/g, and the second is applying a voltage of +1.2 V to the Ti-AC electrode, by which the capacity was further increased to 115.2 mg/g, which was high relative to the capacities of most chemical adsorbents. When a voltage of -1.6 V

was applied, the Ti-AC electrode was easily regenerated without any use of chemicals. The negative voltage provided the driving force for fluoride to overcome the chemical adsorption of fluoride from the electrode surface. No adsorption capacity attenuation occurred after multiple electrosorption–regeneration cycles.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2018.02.112>.

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